Tungsten carbide as electrocatalyst for the hydrogen evolution reaction in pH neutral electrolyte solutions

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ABSTRACT

In this communication we demonstrate that tungsten carbide, WC, is a promising electrocatalyst for the hydrogen evolution reaction in pH neutral electrolytes. In a systematic investigation of mixed catalysts containing different fractions of WC, W_2C, W and WO_2 we show that the performance of the catalyst is proportional to its WC content, whereas W_2C, W and WO_2 play only a minor role. The relationship between WC content and electrocatalytic activity indicates that hydrogen evolution and oxidation are related to similar surface sites preferentially formed on WC. In contrast to anodic conditions, the cathodic polarization diminishes corrosion processes and thus increases the long term stability.

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1. Introduction

The recent considerable increase in research activity and the resulting impressive research progress of microbial fuel cell technology can be largely attributed to the quite elegant opportunity to directly convert chemical energy, contained in wastewater, into electricity – while clearing the water from its load. Recently, further benefits like sulphur [1,2] or nitrogen [3] removal have been reported. It seems reasonable to use such technology not only to produce electricity but also storable fuels like hydrogen [4]. First attempts go back to Kreysa et al. who proposed the combination of (stacked) microbial fuel cells with water electrolysis [5]. One of the greatest disadvantages of this approach was its low energy efficiency of about 11%, caused, e.g., by the irreversibility of the oxygen electrode of the fuel cell.

In 2005 two groups at Wageningen University, Netherlands [6] and Penn State University, US [7], proposed a novel concept in which the two separate devices – microbial fuel cell and electrolyser – are merged to one single device, waiving efficiency consuming parts like the fuel cell cathode [8] and the electrolyser anode. Since the potential delivered by the microbial anode does

not suffice to produce hydrogen at the cathode a certain amount of extra voltage (minimum 0.13 V, in praxis between 0.2 and 0.6 V [6,7,9–12]) has to be applied to reach the reduction potential of hydrogen and to produce hydrogen at sufficiently high rates. Yet, this voltage is very low when compared to the voltage necessary for conventional water electrolysis (in praxis above 1.6 V [9]).

In a series of papers, the groups at Wageningen and Penn State University have improved the performance of their microbial electrolysis cells (MECs) – increasing hydrogen evolution rate, energetic and substrate conversion efficiency [9–13]. However, up to date, in all publications platinum has been used as cathodic hydrogen evolution electrocatalyst. Obviously, due to their high (and still increasing) price as well as their sensitivity towards catalyst poisons, present in the microbial environment (e.g., H_2S), noble metals should be substituted by less expensive and less sensitive materials. Various non-noble materials have been extensively studied for the hydrogen evolution reaction for conventional electrolysers. Most of them – based on metals like nickel and cobalt and their oxides (see e.g., [14–17]), are known to possess only a limited stability at pH neutral conditions (that are essential for the operation of microbial driven devices). One potential catalyst material, non toxic and low priced, is tungsten carbide [18–20]. We have recently introduced tungsten carbide as anodic MFC electrocatalyst for *in situ* fermentation product oxidation [21–23], where it showed a promising catalytic activity. Now we have investigated the ability of the same material to act as an electrocatalyst for the cathodic hydrogen evolution reaction, HER, in microbial electrolysis cells. We have examined the

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relationship between catalyst composition and catalytic activity as well as the stability of the material when used as catalyst for the HER in pH–neutral electrolyte solutions. As a result of this study we can demonstrate that tungsten carbide can be considered as a promising low cost electrocatalyst for hydrogen generation in microbial electrolysis cells.

2. Experimental

2.1. Catalyst synthesis

All WC samples were synthesized from WO_3 (Strem Chemicals, Germany), via a carburization procedure, as described in [21,22]. The basis for this study is a set of 27 individually synthesized samples, as listed in Table 1. The major constituent of all samples is WC, however, most samples also contain various amounts of W and W_2C as side products of the reductive carburization and WO_2, an indicator of an incomplete conversion of the reaction precursor. The deviating composition of the samples can be attributed to the sensitivity of the reaction to variations in the flow rate of carbon monoxide and to small changes in the temperature distribution in the furnace. Although such deviation is usually disadvantageous for preparative procedures, it allows a systematic search for correlations between composition and physical–chemical properties of the catalysts and its electrochemical and electrocatalytic behaviour and was for this reason chosen for this study.

2.2. Electrode preparation

As the electrode substratum, polycrystalline sintered graphite in the form of graphite discs (Ø 4.9 mm, 0.19 cm^2 geometrical surface area) was used. The polycrystalline graphite electrodes (for spectral analysis, Elektrokohle, Lichtenberg, Germany) were paraffin impregnated in order to prevent a soaking with electrolyte solutions [24]. For electrode preparation a defined amount of the tungsten carbide powder (50 mg) was mixed with 5% Nafion®

Table 1
Grain size and chemical composition of the tungsten carbide samples, studied throughout this investigation.

ID	Grain size WC (nm)	Fraction (%)			
		WC	W_2C	WO_2	W
III_01	10.4	100.0	0.0	0.0	0.0
III_02	14.5	45.7	54.3	0.0	0.0
III_03	11.4	100.0	0.0	0.0	0.0
III_04	12.7	22.6	0.0	0.0	0.0
III_05	26.0	100.0	0.0	0.0	0.0
III_06	11.4	100.0	0.0	0.0	0.0
III_07	12.8	89.8	10.2	0.0	0.0
III_08	13.2	27.8	72.2	0.0	0.0
III_09	13.4	90.6	6.6	2.8	0.0
III_10	14.2	49.7	50.3	0.0	0.0
III_11	11.8	18.8	79.3	1.9	0.0
III_12	15.9	63.9	36.11	0.0	0.0
III_13	17.5	53.6	42.9	0.0	3.5
III_14	14.2	78.5	21.5	0.0	0.0
III_15	18.8	38.8	61.2	0.0	0.0
III_16	16.5	12.1	86.6	1.3	0.0
III_17	3.0	3.2	66.3	30.5	0.0
III_18	16.4	34.0	41.2	0.0	24.8
III_19	7.7	71.1	16.0	12.9	0.0
III_20	7.4	48.6	28.3	23.2	0.0
III_21	6.5	82.1	5.7	12.2	0.0
III_22	8.1	92.6	7.4	0.0	0.0
III_23	15.6	66.7	33.3	0.0	0.0
III_24	13.4	73.8	26.2	0.0	0.0
III_25	17.3	27.2	38.7	0.0	34.2
III_26	17.8	95.0	5.0	0.0	1.0
III_27	13.7	96.0	3.0	0.0	0.0

solution and hand-pressed onto the graphite disc. The electrodes were allowed to dry in air at ambient temperature and where then electrochemically characterized.

2.3. Electrochemical characterization

All electrochemical experiments were carried out at room temperature (22–23 °C) as half-cell experiments, mostly using a conventional three electrode set-up. Platinum electrodes served as the counter electrodes and Ag/AgCl electrodes (sat. KCl, Sensortechnik Meinsberg, Germany, 0.199 V vs. SHE, at 23 °C [25]) as reference electrodes. In order to exclude mass transfer limitations of the hydrogen evolution process, all electrochemical data are based on rotating disc experiments. The working electrodes were mounted at a rotating disc electrode device (RDE 616, EG&G, USA) and were rotated at a rate of 1000 rpm. For the determination of the electrocatalytic hydrogen oxidation activity, chronoamperometry (using steady state conditions) and cyclic voltammetry were carried out in nitrogen bubbled electrolyte solution. Control experiments show that hydrogen evolution current density data from cyclic voltammetry (non-Faraday currents being eliminated by averaging forward and backward scan) are comparable to those obtained with chronoamperometry.

The hydrogen evolution process was qualitatively supported by bi-potentiostatic experiments using a four electrode set-up, in which additionally to the working electrode a platinized Pt-wire (set at a constant potential of 0.3 V) as a secondary working electrode was employed as a sensor for the evolved hydrogen.

All experiments were performed using Autolab PGSTAT 20 and 30 potentiostats/galvanostats (Ecochemie, Netherlands). All catalyst samples were examined as three independent electrode replicas.

100 mM H_2SO_4, and 100 mM sodium–phosphate-buffer, pH 7, served as electrolyte solutions. In all experiments, the electrolyte solutions were purged with nitrogen for 15 min prior to the experiments in order to remove oxygen. During the measurements, the headspace of the electrochemical cell was continuously purged with nitrogen.

2.4. X-ray diffractometry

The composition and morphology of the catalyst powder were determined by X-ray diffraction. X-ray powder patterns were recorded using a HZG 4 Diffractometer (Seifert-FPM) in the Bragg-Brentano geometry. CuK_α radiation (40 kV and 40 mA) was applied and an angle range from 15 to 908/2ϑ was recorded at 0.02 increments and with 1 s counting time. The X-ray patterns were identified with the help of the PDF-2® X-ray database (International Centre for Diffraction Data, ICDD) referring to WC (#73-0471), hexagonal W_2C (#79-0743), W (#04-0806) and WO_2 (#86-0314). The mean grain size and the mass percentages of each compound were determined as described in [22].

2.5. ICP OES and Ion chromatography

For the qualitative and quantitative determination of soluble tungsten species ion chromatography (IC) and inductively coupled plasma optical emission spectroscopy (ICP OES) were used. An ICS-1000 (Dionex, Germany) equipped with an Ion Pac AS9 HC column, ASRS-Ultra 4 mm electrochemical cation suppressor and a DS 6 heated conductivity cell was used for ion chromatography. The mobile phase was 12 mM Na_2CO_3 and 10 mM $NaHCO_3$. The ICP OES was performed with an Optima 2100 series spectrometer (PerkinElmer, USA). The samples were diluted 1:10 before measurement and measured in nine replicas. The standard deviation was always less than 5%.

3. Results and discussion

3.1. Electrocatalytic behaviour

Fig. 1 illustrates the hydrogen evolution behaviour of tungsten carbide, in comparison to unmodified graphite and to platinum, under acidic condition (Fig. 1A) and at neutral pH (Fig. 1B). For a better evaluation of the experimental results, the figures are plotted with two x-axes, the lower axes providing the electrode potential, with respect to the potential of the reference electrode, the upper axes depicting the overpotential of the hydrogen evolution reaction, $\eta_{H_2/2H^+} = E^{\theta'}_{H_2/2H^+} - E_{electrode}$. Here $E^{\theta'}_{H_2/2H^+}$ represents the reversible hydrogen potential, which, by using the respective pH and a hydrogen partial pressure of 1, was calculated to be -606 mV (vs. Ag/AgCl; equal to -407 mV vs. NHE) for pH 7 electrolyte solutions and -238 mV for 0.1 M H_2SO_4.

Fig. 1A clearly shows that (as expected) for acidic conditions, platinum is the superior hydrogen evolution catalyst with a HER current density of -226 mA cm^{-2} at an overpotential of 760 mV (corresponding to a potential of -1 V vs. Ag/AgCl) and -84 mA cm^{-2} at $\eta = 300$ mV. With a maximum current density of -118 mA cm^{-2} ($\eta = 760$ mV) and 26 mA cm^{-2} ($\eta = 300$ mV) the electrocatalytic

activity of tungsten carbide is significant, though it reaches only 31% (at $\eta = 300$ mV) of the activity of platinum.

At neutral pH, the performance of all materials is considerably lower than under acidic conditions – a result that is to be expected and that has already reported for the cathodic oxygen reduction under microbial fuel cell conditions [8]. Thus, after base line corrections of the respective cyclic voltammograms (Fig. 1B), for $\eta = 300$ mV, effective hydrogen evolution current densities of -15.2 and -8.8 mA cm^{-2} are achieved for platinum and tungsten carbide, respectively. Yet, these values show that at neutral pH tungsten carbide reaches about 57% of the current densities obtained with platinum. When compared to the acidic conditions, where WC reached only 31%, the performance of tungsten carbide at neutral pH is satisfactory. It may be speculated that the kinetics of the hydrogen evolution reaction at neutral pH is less hampered at tungsten carbide catalysts than it is at platinum.

In literature, different tungsten compounds have been reported to possess hydrogen evolution capabilities. To investigate, which tungsten species is the most suited for microbial electrolysis cells, we have studied catalyst samples of different composition with respect to their hydrogen evolution performance. Fig. 2 summarizes the catalytic behaviour of different catalyst samples as a function of their composition (molar fractions of their constituents). It can be clearly seen that with increasing WC content higher HER current densities are achieved. The current densities for catalyst samples with low electrocatalytic activity correspond very well with the data for pure WO_3 (as used as the precursor for the WC preparation). W_2C and WO_2, on the other hand, do not significantly contribute to the hydrogen evolution process (data not plotted). These findings are in good agreement with our previously published data, which showed a direct correlation between the hydrogen oxidation performance of mixed tungsten oxide/carbide catalysts and their WC contents [21].

It seems legitimate to assume that hydrogen evolution and oxidation are taking place at the same surface sites, via the same mechanism (but in the reverse direction). This is supported by Sokolsky et al. [26] who analyzed the kinetics of the hydrogen evolution and oxidation on plane tungsten carbide disk electrodes and showed that hydrogen oxidation and evolution proceed on WC – with the proton (de)sorption being the rate limiting step. Further, our results are supported by Armstrong and Bell [20] who found that in acidic electrolyte solutions WC possessed a 100 mV higher
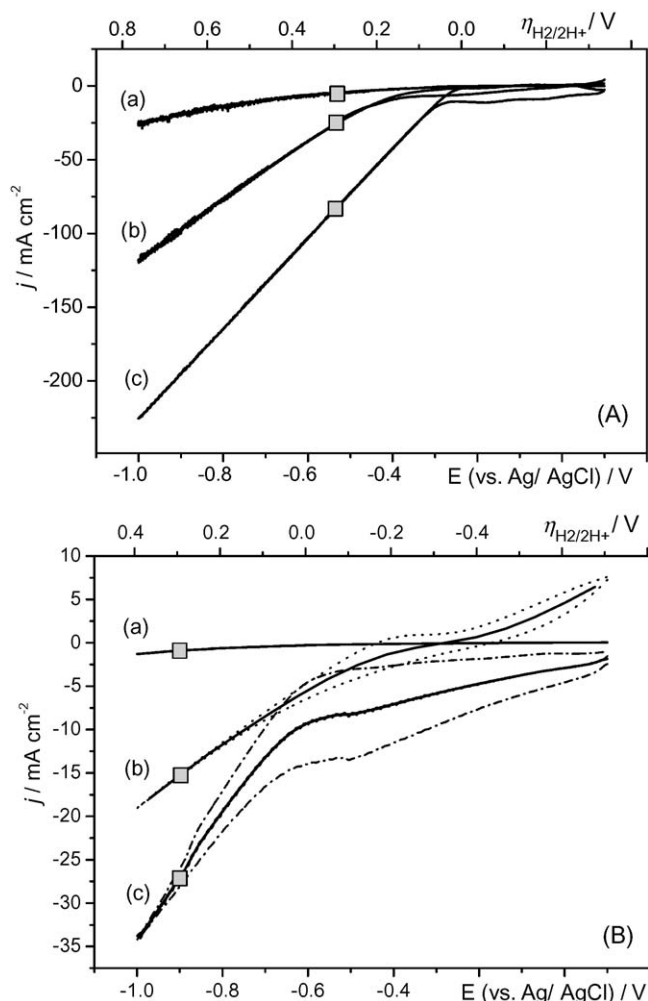

Fig. 1. Cyclic voltammograms of the hydrogen evolution reaction at (a) polycrystalline graphite, (b) tungsten carbide (sample III_16), and (c) Vulcan XC-72 20% Pt. The electrolytes were (A) 100 mM H_2SO_4, and (B) 100 mM, pH 7, phosphate buffer. The scan rate was 5 mV s^{-1}. The solid lines in (B) represent the arithmetic mean of forward and backward scan used for elimination of non-Faraday currents.
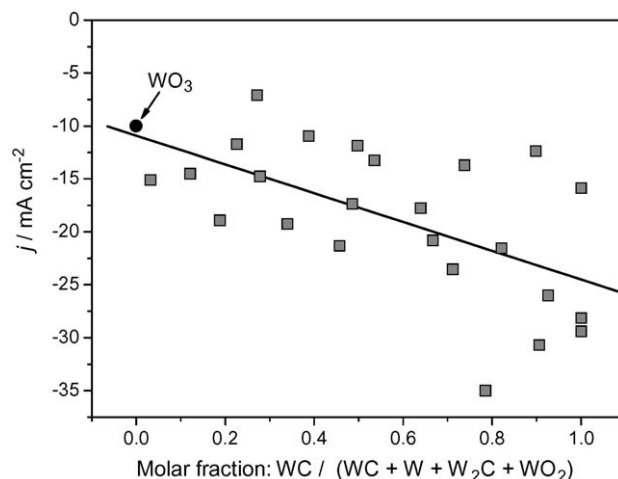

Fig. 2. Dependence of the hydrogen evolution current densities of different catalyst samples on their composition, as derived from X-ray powder analysis. The current values are based on steady state chronoamperometric experiments, performed at -1 V (vs. Ag/AgCl) electrode potential, in 0.1 M phosphate buffer pH 7. All data represent the arithmetic means of three independent electrode replicas. The mean standard variation of the current density data was 10%.

Table 2
Corrosion rates of tungsten carbide in different electrolytes and under different polarization conditions.

Electrolyte (0.1 M)	Corrosion rate[*] (mol [W] h^{-1} cm^{-2})	
	0.2 V[**] (vs. Ag/AgCl)	−1.0 V (vs. Ag/AgCl)
H$_2$SO$_4$ (pH 0.69)	∼3.6 × 10^{-7}	∼2.4 × 10^{-9}
pH 3[***]	∼4.3 × 10^{-7}	∼6.3 × 10^{-8}
pH 7[***]	∼3.8 × 10^{-6}	∼8.2 × 10^{-8}

[*]The data are average values of the samples III_10, III_11. III_12, III_13, III_14 and III_19; [**]from Ref. [21]; [***]phosphate buffer.

overpotential than Pt for the HER, but W$_2$C:WC (7:3) mixtures showed an even increased overpotential and a thus worse performance. On the other hand, our results contradict Ma et al. [27] who reported that W$_2$C electrodes showed a higher HER catalytic activity than WC electrodes; the latter, however, showing better hydrogen oxidation performance.

3.2. Corrosion behaviour of tungsten carbide

Since the long term stability and performance of an electrode material is of utmost importance for its technical applicability we have examined the stability of tungsten carbide electrodes as hydrogen evolution catalyst at neutral pH. As already reported in our previous work [21], at neutral pH tungsten carbide undergoes a slow oxidative dissolution (formation of soluble WO$_4$$^{2-}$ as the oxidation product of WC, WO$_3$) – even when stored in purely anoxic electrolyte solution. The corrosion rate increases with increasing pH and in the presence of phosphate anions due to the formation of soluble heteropolytungstates. Additionally, when polarized at a positive potential, a significant increase of the dissolution process takes place.

Table 2 depicts a comparison of the dissolution rates of tungsten carbide under anodic (as used for hydrogen oxidation) and cathodic polarization (as used for HER). From this table the following conclusions can be drawn: At all potentials the dissolution rate increases with the pH. This fact can be attributed to the increasing solubility of WO$_3$ (especially in the presence of phosphate) at higher pH values. At negative polarization, the dissolution rate is considerably slower than at positive polarization. The factor may be as high as 150 for acidic conditions and 46 for pH 7. Yet, it has to be stated that especially at higher pH values and in the presence of larger concentrations of phosphate ions a slow corrosion process cannot completely be suppressed.

4. Conclusion

Although not being able to completely match the performance of the precious metal platinum, tungsten carbide, WC, is an interesting alternative to platinum for the cathodic electrocatalytic hydrogen evolution in microbial electrolysis cells. In comparison to other tungsten compounds like W$_2$C, WO$_3$ and WO$_2$ it possesses the highest HER performance. This finding is in line with our previous data for the electrocatalytic hydrogen oxidation, which may suggest similar or identical reaction mechanisms. From the knowledge on the hydrogen oxidation at WC it may also imply the rate of the hydrogen sorption/desorption – a process strongly dependent on the tungsten carbide surface chemistry and groups – to be the limiting factor for both the hydrogen evolution and oxidation reactions.

Acknowledgements

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